Novel magnetic chitosan/graphene oxide/activated carbon composite beads for the removal of nonsteroidal anti-inflammatory pharmaceutical compound (Diclofenac) from aqueous solutions

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The ongoing discovery of pollutants of emerging concern (ECs) in wastewaters has received an increasing amount of attention in recent years [Patel et al. (2019)]. Removal of them from water and wastewater is of major significance due to their widespread use and detrimental effects on aquatic assemblages and population health. Furthermore, one of the main problems these days is that ECs are discovered in drinking waters in addition to their discovery in the atmosphere, sewage, ground, and various aquatic matrices. The concentration of pharmaceutical compounds in wastewater may range between ng/L and μg/L [Rasheed et al. (2020)]. The World Health Organization (WHO) is highlighting the importance of the applied process for the removal of pharmaceuticals due to their pseudo-persistent nature and the estimated yearly usage of several hundred tons in affluent nations [Rizzo et al. (2019)]. Furthermore, these compounds are continuously released into the aquatic environment since the biological treatment methods used in wastewater treatment plants (WWTPs) cannot effectively break them down.

The amount of pharmaceuticals consumed worldwide has increased by about three times in the last 30 years. Analgesics and anti-inflammatories are among the most commonly used classes of drugs, and they are frequently found in wastewater and water samples [Gkika et al. (2023)]. Several studies have shown that the consumption of analgesic compounds has increased and that WWTPs have not completely removed them. The model pollutant of the present study (diclofenac) belongs in the category of the frequently used nonsteroidal anti-inflammatory drugs (NSAIDs), which usage is basically in treating inflammation or musculoskeletal pain and they can be delivered in aquatic systems through several ways, such as hospitals, health centers or pharmaceutical plants [Lonappan et al (2016)]. According to the literature, concentrations up to 5164 ng L^{-1} DCF were detected [Kosma et al. (2014)].

Various technologies and methods have been investigated for the elimination of pharmaceuticals from drinking- water treatment plants, groundwaters, industrial and hospital wastewaters, and aquatic systems. These include ion exchange, coprecipitation, filtration, reverse osmosis, Fenton oxidation, biodegradation, ozonation, and electrochemical reduction. The primary drawbacks of these technologies are their cost and practical application complexity, as well as the occasional requirement for the use of additional, frequently dangerous chemical reagents that result in processes that are not environmentally benign. On the other hand, adsorption-based remediation techniques, are more in line with the ideas of sustainable development and green chemistry. Therefore, it is assumed that adsorption techniques are practical, adaptable, and mainly affordable [Sophia A. & Lima (2018)]. In advance, the performance of an adsorption process is affected by the ability of using various adsorbents characteristics and the interest for its application on pharmaceutical compounds [Malesic-Eleftheriadou et al. (2021)].

Given the need for sustainable materials, there has been a rising interest in employing polymers derived from renewable resources within the past ten years. In this light, this study presents a novel composite material, consists of chitosan (Cs), graphene oxide (GO) and activated carbon produced from biomass (AC) with the combination of magnetic particles. The magnetic particles were used to separate the mass of adsorbent material easily for the different adsorption-desorption cycles. In recent years the scientific community has turned its interest to chitosan because it is non-toxic, biodegradable and it has a low cost. The natural biopolymer chitin is the source of chitosan, and the adsorption capacity of chitosan depends on the chitin source. As a matter of fact, the degree of chitosan's deacetylation (DD) and polymerization determines its most significant uses [Kyzas et al. (2017)]. The ability to moderate at movable locations within the molecule to boost adsorption capability is one of the best features for the synthesis of chitosan derivatives. The most common alteration reactions on chitosan molecules are grafting and cross-linking [Kyzas & Bikiaris (2015)].

Therefore, we exploited the sight of grafting Cs, to synthesize a new composite with better properties, using GO and AC. As a two-dimensional byproduct of oxidized graphene sheets, graphene oxide (GO) is perhaps one of the most studied carbon nanomaterials for environmental applications. It is an inexpensive material with a vast surface area and modification potential, but because oxygen molecules are integrated, it has less mechanical properties than pure graphene. Conversely, the material is becoming more hydrophilic, or soluble in aqueous solutions, due to the presence of carboxylic and hydroxylic acid groups [Majumder & Gangopadhyay (2022)]. Due to particle aggregation, one drawback of GO is that it cannot always remove a large amount of chemical contaminants through adsorption; however, this can be addressed by making a number of adjustments. But, when graphene oxide particles are added to CS, chitosan's mechanical strength can be increased without affecting its antibacterial properties [Malesic-Eleftheriadou et al. (2023)].

With their high specific surface area, total pore volumes, and excellent adsorption capability, activated carbons (ACs) are a class of materials that can be divided into three groups based on their porous structures: microporous (0–2 nm), mesoporous (2–50 nm), and macroporous (>50 nm) [Zhang et al. (2010)]. It is crucial to emphasize the concept of activated carbon, which is a carbon-rich solid produced by pyrolysis from biomass or other carbonaceous materials. A carbon material is also "activated" in the process by procedures that significantly expand its surface area, which enables it to absorb a greater number of molecules. Activated carbon is usually used in remediation or purification projects because of its strong adsorption capacity, which makes it useful in eliminating pollutants from air and water. So, using the most suitable primary source to generate activate AC with the highest specific surface, meaning the best adsorption capacity, is crucial when using AC in remediation and decontamination technologies [Liakos et al. (2021)].

The composition and morphology of new novel material was characterized before and after adsorption, by using Fourier Transform Infrared spectroscopy (FTIR), X-ray diffraction (XRD), Scanning electron microscopy (SEM) and BET analysis. Then, batch adsorption experiments were conducted, for application and evaluation of this composite material. The effect of pH, contact time, initial concentration, temperature and initial mass of adsorbent were tested. Pseudo-first and pseudo-second order equations applied in order to study the adsorption kinetic mechanism of diclofenac on the produced beads. Freundlich and Langmuir isotherm models fit to draw conclusions regarding the distribution of adsorbent between liquid and adsorbent. Overall, chitosan/activated carbon/graphene oxide composite showed promising prospects as an effective and environmentally friendly approach for the removal of pharmaceutical residues from wastewater.

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